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ON THE QUESTION OF THE NATURE OF THE CHANGE IN THE VIBRATIONAL FREQUENCIES OF SCN AND SeCN GROUPS UPON COORDINATION

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The XCN groups (X = S, Se) form coordination bonds of various types

$$\mathrm{XCN-M}\quad \text{(I)}; \qquad \mathrm{NCX-M}\quad \text{(II)}; \qquad \mathrm{M-NCX-M}\quad \text{(III)}.$$

Here M is the atom of the metal—the complex-forming agent. Crystal-structure studies show that the CNM angle lies within 150-180°, and the CXM angle within 90-120°. It has been established ([1–19]) that different structures I-III correspond to different vibrational frequencies. The two frequencies of the stretching vibrations of the linear ion SCN^- are $\nu(CN) \approx 2050$-2060 and $\nu(CS) \approx 750$ cm^{-1}.* For structure I, $\nu(CS)$ increases, compared with the ion, to ~ 800 cm^{-1}; for structure II it decreases to ~ 700 cm^{-1}, while for structure III it either increases or decreases. $\nu(CN)$ is increased for all structures; the maximum increase (by $\sim$ 70-120 cm^{-1} ([10])) has been found for structure III. The frequencies of the stretching vibrations of the $SeCN^-$ ion, found ([20]) in the spectrum of KSeCN at 77° K, are: $\nu(CN) = 2072$ and $\nu(CSe) = 559$ cm^{-1}. Information on the vibrational frequencies of SeCN groups is limited; the available data ([15–19]) show that in complexes with SeCN groups the same regularities are observed: $\nu(CSe)$ for structure I increases, compared with the $SeCN^-$ ion, to $\sim$ 605-672 cm^{-1}, while for structure II it decreases to $\sim$ 520-543 cm^{-1}; $\nu(CN)$ for structures I and II, as a rule, is increased (although a decrease is sometimes observed); in complexes with structure III, $\nu(CN)$ is increased to $\sim$ 2130-2140 cm^{-1}.

In studying the spectra and structures of compounds with XCN groups, two questions arise: 1) what is the nature of the change in frequencies on going from XCN^- ions to coordinated groups, and 2) what changes do the XCN groups undergo upon coordination? The causes of the frequency change may be different. Redistribution of the electron cloud upon coordination may lead to a change in the force constants of the CX and CN bonds. Of course, redistribution of the

electron cloud upon coordination always occurs; but it is not known whether the observed changes in frequencies are determined by this redistribution. The change in frequencies may be determined predominantly by the influence of other parameters, with the force constants of the CN and CX bonds remaining practically unchanged; such changes we shall call a "change in the vibrations of the system" on going from XCN^- ions to structures I-III. We attempted to clarify the questions posed by means of an approximate analysis of the vibrations of various models corresponding to structures I-III.** For simplicity, models with one XCN group were chosen, since the regularities in the frequency changes do not depend on the number of XCN groups in the complex. The analysis was carried out by the method,

* Here and below, the designations of the frequencies ν(CN), ν(CS), etc., indicate the bond that is maximally deformed in the vibration with the given frequency; these designations have the advantage that they are applicable both to ions and to structures I-III, irrespective of the symmetry of the molecule or of the vibration.

** A detailed description of the work will be set forth in the *Journal of Inorganic Chemistry*.

analogous to that used in the case of nitriles ([21]). The vibrational frequencies and modes of vibration were calculated. The influence of the various factors was investigated separately. At first, the influence of redistribution of the electron cloud was deliberately excluded (the internal force constants of the XCN groups were taken as unchanged and equal to the constants of the ions XCN^-). The calculated frequencies were then compared with those found experimentally. Linear models XCN–M, MCX–M, M–NCX–M and nonlinear NCS–M with CSM angles equal to 90 and 120° were analyzed. Analysis of the SCN group showed that, in order to determine the character of the frequency changes, it is sufficient to restrict oneself to the study of linear models; therefore, in cases involving SeCN groups and bridging SCN groups, only linear models were considered. Such a simplification of the problem affects the absolute values of the calculated frequencies, but not the character of their changes. The solution was carried out in natural coordinates corresponding to changes in the lengths of the CN, CX, NM, XM bonds and in the NCS and CSM angles. The mass m of the M atoms was varied from 50 to 200 (in atomic-weight units). The following values of the force constants were used (in mdyn/Å):

a) **SCN group:** $k_{CN} = 15.35$; $k_{CS} = 4.96$; $k_{CS,CN} = 0.9$ (with these values of the constants, for the ion, ν(CN) = 2046 and ν(CS) = 748 cm^{-1} were calculated; in the spectrum of an acetone solution of KSCN ([10]), ν(CN) = 2050 and ν(CS) = 748 cm^{-1} were found); $k_\alpha / r_{CN} r_{CS} = 0.300$, where k_α is the deformation constant of the SCN angle, $r_{CN} = 1.17$ Å and $r_{CS} = 1.61$ Å are the CN and CS bond lengths, taken according to Jones ([22]); for the SM bond length, $r_{SM} = 2.5$ Å was adopted. The force constants of the MN and NS bonds were varied from 0.5 to 4.0. The remaining dynamic

coefficients were varied within certain limits or were taken equal to zero (in particular, the coefficients of dynamic interaction of bonds having no common atoms).

b) **SeCN group:** $k_{CN} = 15.1$, $k_{CSe} = 3.88$; these constants were calculated ([20]) from the frequencies found in the spectrum of KSeCN, under the assumption of the simplest valence-force field. The interaction coefficient $k_{CN,CSe}$ was taken equal to zero or was varied within the range 0.1–0.9. The force constants of the MN and SeM bonds were varied from 0.5 to 4.0. The remaining dynamic-interaction coefficients were taken equal to zero.

Altogether, more than two hundred secular equations were formulated and solved. The results obtained show the following.

1. **Structure I.** When XCN groups are coordinated through nitrogen atoms, ν(CN) and ν(CX) increase even when the force constants of the CN and CX bonds remain unchanged. The frequencies ν(CN) are practically independent of the mass of the M atom; ν(CX) decreases slightly with increasing mass of the M atom. An increase in the interaction coefficient $k_{CX,CN}$ lowers ν(CN), but has almost no effect on ν(CX); a change in the interaction coefficient $k_{MN,CN}$ has little effect on ν(CN) and practically none on ν(CX). Consequently, the frequencies ν(CX) depend less on nondiagonal force coefficients than do the frequencies ν(CN). In all vibrations all bonds are deformed, although not to the same extent. In the vibration with frequency ν(CN), the CN bond is deformed more than the other two. In the vibration with frequency ν(CX), the CX and MN bonds change predominantly, but the CX bond is deformed to the greatest extent. In the vibration with frequency $\nu_3(A) = \nu$(MN), the MN bond is deformed most of all, the CX bond less, and the CN bond still less. The forms of vibration are almost independent of the mass of the M atom, but change somewhat with a change in the force constant of the MN bond. In the valence vibrations of the ions XCN^-, both XC and CN bonds are substantially deformed. Thus, if the internal force constants upon coordination of XCN groups remained unchanged, then the frequencies ν(CN) and ν(CX) would increase; the magnitude of the increase, for permissible values of the force constant of the MN bond, is approximately the same as that observed experimentally. Consequently, in the realization of structure I, an increase in the force constants of the CN and CX bonds is not necessary, despite the rise of ν(CN) and ν(CX).

In other words, upon coordination of XCN groups through nitrogen atoms, almost no change occurs in the force field of the XCN^- ions, and the experimentally observed increase in the frequencies is due mainly to a change in the mechanics of the vibrations of the system. An indirect indication of the absence of substantial changes in the CN and CX bonds is provided by the stereochemistry of the MNCX groups. The closeness of the MNC angle to 180° suggests that the M–N bond is formed

Figure 1

Figure 1: Figure 1

Fig. 1. Change in vibrational frequencies as a function of changes in the force constants of the MN and MS bonds of coordinated SCN groups*: **a**) Change in ν(CN). 1 –linear model S–C–N–M (circles) and M–S–C–N–M at $k_{MS} = k_{MN}$ (crosses); 2 –linear model N–C–S–M; 3 –nonlinear model N–C–S–M. In all cases the mass $m = 50$; **b**) Change in ν(CS). 1 –linear model S–C–N–M; 2 – linear model N–C–S–M; 3 –nonlinear model N–C–S–M at $\angle$CSM = 120°; 4 –nonlinear model N–C–S–M at $\angle$CSM = 90°; 5 –linear model M–S–C–N–M at $k_{MS} = k_{MN}$. In all cases the mass $m = 50$; **c**) Change in ν(MN) of the linear model S–C–N–M; **d**) Change in ν(MS) of the model N–C–S–M. 1 – $\angle$CSM = 180°; 2 –$\angle$CSM = 120°; 3 –$\angle$CSM = 90°. In all cases $m = 50$.

formed through the lone pair of *s*-electrons of the N atom (and not the π-cloud of the entire NCX group), which apparently leads only to minimal changes in the electron density in the N–C and C–X bonds. With the aid of the obtained graphs (see Fig. 1), one can estimate the force constants of MN bonds in complexes with structure I. For this purpose it is better to use the frequencies ν(CX), since they are more sensitive than the frequencies ν(CN) to changes in the force constants of the MN bonds and depend less on the off-diagonal force coefficients. The estimation of the force constants of the bonds is meaningful, for example, when comparing isorhodanide and isoselenocyanate complexes. Thus, an estimate carried out [19] for complexes trans-[M(NCX)$_2$A$_4$], where M = Ni,

* Analogous curves were obtained for SeCN groups.

Co or Mn, and A is a dimethylformamide molecule, showed that the bonds of the M atoms with the SCN groups are stronger than those with the SeCN groups.

2. Structure II. With unchanged force constants, coordination of the XCN$^-$ groups through the X atoms has no effect on the frequencies ν(CN), which remain practically unchanged. ν(CX) increases, but less than in structure I; the increase in ν(CX) is the greater, the larger the CXM angle (within the range 90—180°). ν(CN) is practically independent, and ν(CX) depends only slightly, on the mass of the M atom. An increase in the interaction coefficient $k_{\mathrm{CX,CN}}$ lowers ν(CN), but has little effect on ν(CX). Thus, if the force constants of the CX and CN bonds remained unchanged upon coordination, then ν(CN) would practically not change, while ν(CX) could increase. Experiment, however, shows an increase in ν(CN) and a decrease in ν(CX). This means that, upon coordination through the X atoms, such a change in the force constants occurs that the force constants of the CX bonds decrease (the CX bond approaches a single bond), while those of the CN bonds increase somewhat in comparison with the XCN$^-$ ions. (It is not difficult to show that the other variants of changes in k_{CN} and k_{CX} do not satisfy the experiment.) The results of structural studies

agree with this interpretation. The closeness of the CXM angle to 90° means that the X–M bond is formed at the expense of the π-electron cloud of the NCX group; as a result, the CX bond is somewhat weakened, while the CN bond is strengthened.

3. Structure III. With unchanged internal force constants, the transition from XCN^- ions to structure III leads to almost the same increase in ν(CN) as in structure I; this frequency does not depend on the force constant of the MX bond. ν(CX) increases upon coordination. ν(CN) is independent, while ν(CX) depends only weakly on the masses of the M atoms. In all valence vibrations all bonds are deformed, but not to the same degree.

Thus, if the internal force field of the XCN groups remained unchanged upon formation of structure III, then ν(CN) would change in the same way as in structure I, while ν(CX) would increase. Experiment shows, however, that ν(CN) increases more than in structure I, while ν(CX) sometimes increases and sometimes decreases. This becomes understandable if one takes into account that structure III has the properties of structures I and II. The increase in ν(CN) in this case is explained by the simultaneous change in the mechanics of the vibrations of the system and the increase in the force constant of the CN bond; the action of both factors is expressed, in sum, in the greatest increase of ν(CN) in comparison with structures I and II. The frequency ν(CX) in bridging groups may either increase or decrease, depending on which of two oppositely acting factors–the decrease in the force constant of the CX bond or the change in the mechanics of the vibrations of the system–predominates.

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Note: Figure translations are in progress. See original paper for figures.